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# Relative Photoionization Cross-Sections of Super-Atom Molecular Orbitals (SAMOs) in C<sub>60</sub>

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# Relative Photoionization Cross-Sections of Super-Atom Molecular Orbitals (SAMOs) in C<sub>60</sub>

## ABSTRACT

The electronic structure and photo-induced dynamics of fullerenes, especially C<sub>60</sub>, is of great interest since these molecules are model systems for more complex molecules and nanomaterials. In this work we have used Rydberg Fingerprint Spectroscopy to determine the relative ionization intensities from excited SAMO (Rydberg-like) states in C<sub>60</sub> as a function of laser wavelength. The relative ionization intensities are then compared to the ratio of the photoionization widths of the Rydberg-like states, computed in time-dependent density functional theory (TD-DFT). The agreement is remarkably good when the same photon order is required to energetically access the excited states. This illustrates the predictive potential of quantum chemistry for studying photoionization of large, complex molecules as well as confirming the assumption that is often made concerning the multiphoton excitation and rapid energy redistribution in the fullerenes.

## Introduction

Gas phase photoelectron spectroscopy provides a powerful tool to probe in detail the fundamental electronic structure and photo-induced dynamical properties of isolated molecules.(1) The advent of new light sources such as tunable ultrafast laser systems or Free Electron Lasers is providing ever more advanced possibilities for experimentally probing photo-induced electron dynamics on increasingly complex systems.(2) For planning and reliably interpreting the results of such advanced experiments, it is essential to develop theoretical methods that are able to accurately predict the outcome so that we understand the nuances and fundamental factors involved in taking such a measurement. This work focuses upon the comparison of experimental measurements and theoretical predictions of photoionization cross-sections from excited electronic states of a complex molecule,  $C_{60}$ . It has recently been suggested that there could be significant challenges in interpreting femtosecond (fs) photoionization experiments as the detection sensitivity could significantly depend on changes in the photoionization cross-section as the system evolves.(3) Fullerenes are interesting model systems to help develop both the new experimental possibilities and the associated theoretical techniques. The high symmetry of  $C_{60}$ , making it accessible for high level theoretical investigation, combined with its interesting electronic properties and ease of experimental handling,(4) provides an attractive but challenging subject for study.

In earlier studies it has been shown that one-colour fs photoelectron spectra of gas phase fullerenes typically show 3 or 4 prominent peaks corresponding to binding energies in the range of 1-2 eV, superimposed on a thermal electron background.(5-7) Theoretical photoionization angular distributions of a band of 500 neutral excited states computed in TD-DFT confirmed that

the peaks observed in the photoelectron spectra are due to single photon ionization from excited “SAMO” (Super-Atom Molecular Orbital) states.(6, 8) The SAMO states are singly excited states where an electron is (indirectly) promoted from the highest occupied molecular orbital (HOMO) to a ‘SAMO’ s, p or d orbital. The SAMOs in fullerenes were first identified in low-temperature scanning tunnelling spectroscopy studies of  $C_{60}$  on a copper surface and described as diffuse Rydberg-like orbitals with the charge distribution centred on the centre of the hollow carbon cage.(9) They can be considered as low-lying mixed Rydberg/valence states with a dominant Rydberg contribution(10) and significant charge density within the cage.(8) The high symmetry and hollow character of  $C_{60}$  leads to the beautiful and simple atomic nature of the Dyson orbitals of the SAMO states, shown in Fig. 1, and a correspondingly distinct photoelectron angular distribution for the s-orbitals.(8) The Dyson orbitals are one-particle orbitals computed as the overlap between the neutral and cation many-electron wavefunctions and represent the probability amplitude of the electron that is ionized.(8, 11) They are used to calculate photoionization intensities and photoelectron angular distributions, as described in detail for  $C_{60}$  in an earlier publication.(8) For  $C_{60}$  the SAMO Dyson orbitals are very similar to the SAMO molecular orbitals.

The prominence of the SAMO peaks and the development of the thermal background in the photoelectron spectra(4) was attributed to the much larger photoionization widths (orders of magnitude larger than for the valence states) that were predicted for the SAMO states for the low photon energies used in the experiments.(8) These large photoionization widths are consistent with the recent observation of the correlation between photoionization cross-section and polarizability volume for a range of organic molecules.(3) The predicted photoionization widths for the fullerene SAMOs corresponded to ionization lifetimes on the order of 10 fs while the

ionization lifetimes of non-SAMO states (including the valence states) were predicted to be on the order of ps-ns and thus considerably longer than the laser pulse duration.(8)

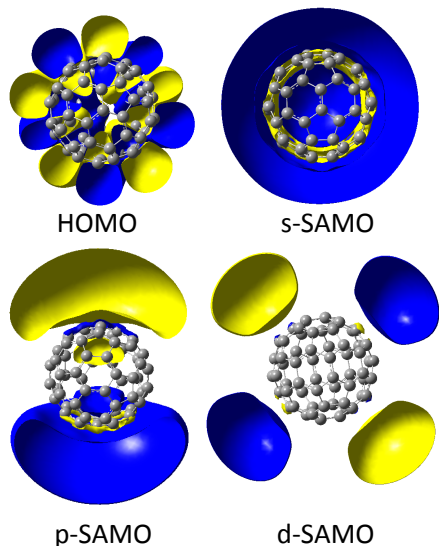


Fig. 1. Cuts in the isocontour amplitudes ( $0.002|e|/a_0^3$ ) of the HOMO and Dyson orbitals of the s, p and d SAMO states of  $C_{60}$ . The electronic structure of the 500 lowest excited states was computed at the TD-DFT/CAM-B3LYP/6-31(+)G(d)-Bq(6-31(6+)G(d)) level. Computational details given in Ref. 8.

In the work presented here, we report photoelectron spectra obtained for a wider range of laser wavelengths than previously reported. We determine the relative photoionization intensities from the SAMO states as a function of laser wavelength and compare them to calculations of the photoionization widths (proportional to the photoionization cross sections) using the TD-DFT approach described previously.(8) This provides an additional stringent test of the theoretical calculations and the very good agreement between experiment and theory illustrates the predictive detail that can be captured for complex polyatomic systems. In addition, the results

provide strong support for the very rapid energy redistribution within fullerenes that is often invoked to interpret experimental results.(12)

## **Experimental and Theoretical Methods**

Photoelectron spectra were obtained using a velocity map imaging spectrometer based on the design of Parker and co-workers.(13) The experimental apparatus has been described in more detail previously.(4, 14)  $C_{60}$  (99.95% purity, SES Research) was introduced into the vacuum chamber as an effusive molecular beam produced by heating the sample in an oven to  $\sim 500$  °C.

A regenerative amplified Ti:sapphire laser system (800nm fundamental output, pulse 110 fs duration) was used to pump a commercial non-collinear optical parametric amplifier (NOPA) providing a tunable light source in the visible range. The pulse durations were sub-100 fs at the interaction region and wavelength dependent. Data provided in the Supporting Information shows that the pulse duration does not significantly influence the results in the range accessed in these experiments (ca. 30 – 90 fs, Fig. S2 and S3). For experiments involving 800 nm or 400 nm light, the NOPA was by-passed, and the 800 nm light was frequency doubled using a 0.5 mm thick BBO crystal cut at 29°. The laser intensity and polarization were controlled using a combination of a half-wave plate and a Glan-laser polarizer and focused into the chamber using a 30 cm focal length, fused silica lens. The laser intensity was chosen for each wavelength to provide a good signal to noise ratio in the photoelectron spectra while ensuring that fragmentation and double ionization peaks were of negligible intensity in the corresponding mass spectra. It was typically within the range  $10^{11} - 10^{12}$  Wcm<sup>-2</sup>.

The laser intersects the effusive molecular beam at right angles and the photoelectrons are extracted using a set of electrostatic lenses and detected using an integrated 40 mm dual

MCP/Phosphor detector (Photonis, ADP 3040FM 12/10/8 60:1). The image is recorded using a CCD camera (AVT, Stingray Model F146B), controlled via a LabVIEW program. The recorded images were centroided(15) and integrated for  $10^6$  -  $10^7$  laser shots. Once recorded, the images were inverted using a POP inversion algorithm,(16) which was modified to include Legendre polynomials up to the  $10^{\text{th}}$  order. The conversion from velocity to energy was calibrated using the well-known peaks from multiphoton ionization via Freeman-type resonances in Xe.(17)

The peaks in the photoelectron spectra were fitted using Lorentzian functions (with 2 functions with small energy separations used to get an optimum fit for the p- and d-SAMO bands, in agreement with the slight splitting of these bands observed in the calculations).(8) The binding energies and peak widths were not changed for fitting the spectra obtained for different laser wavelengths, only the relative intensities. The error bars indicate the uncertainty in both the subtraction of the thermal background and the Lorentzian peak fits.

The details of the theoretical calculations have been presented in a previous publication.(8) Briefly, the electronic structure of the 500 lowest excited states of neutral  $C_{60}$  was computed at the TD-DFT/CAM-B3LYP/6-31(+)G(d)-Bq(6-31(6+)G(d)) level. The binding energies of the first s, p, d and second s band of SAMO states as well as the predicted photoelectron angular distributions were shown previously to be in good agreement with the experimental values.(8) In the photoionization process, the Dyson orbital represents the probability amplitude of the electron that is ionized. The calculated photoionization width is the square modulus of the dipole coupling between the Dyson orbital,  $\phi_I^{\text{Dyson}}$ , and the outgoing plane wave,  $\mathcal{E}_\Omega$ , integrated over the emission angle of the ejected electron,  $\Omega$ , and multiplied by the density of plane waves at the energy of the emitted electron  $\rho(\epsilon)$ .



$$\Gamma_I(\varepsilon) = \rho(\varepsilon) \int d\Omega \left| \langle \varepsilon_\Omega | -\mathbf{E} \cdot \mathbf{r} | \phi_I^{Dyson} \rangle \right|^2 \quad (1)$$

The photoionization widths between the electronic states and the ground state of the cation (five-fold degenerate) were computed using a basis of orthogonalized plane waves to describe the wavefunction of the ionized electron. The photoionization width was computed for each state taking into account the random orientation of the C<sub>60</sub> molecule with respect to the electric field. An electric field of  $4.7 \times 10^6 \text{ Vcm}^{-1}$  was used for the calculations, corresponding to a laser intensity of  $3 \times 10^{11} \text{ Wcm}^{-2}$ , similar to the values used in the experiments. Detailed information on the theoretical methodology is available in Ref. 8. Note that the ionization width,  $\Gamma_I$ , is proportional to the photoionization rate and directly related to the photoionization cross-section. It does not refer to the width of the peaks in the experimental photoelectron spectra.

In order to compare the experimental results with the theoretical predictions, we calculated the ratios of the experimental SAMO peaks for a given laser wavelength and compared them to the calculated ratios of the photoionization widths for the corresponding SAMOs at the appropriate electron kinetic energies. Since we are comparing ratios, the laser electric field term cancels and we can compare data sets taken at different laser intensities. Systematic studies of the influence of fluctuations in experimental parameters, such as laser pulse duration, laser intensity and fullerene oven temperature, were carried out to check that these do not influence the value of the determined intensity ratios. These studies are documented in the Supporting Information.

## Results and Discussion

The experimental photoelectron spectra, Fig. 2 and Supplementary Information (SI) Fig. S1, show the presence of peaks corresponding to ionization from the SAMO states independent of the excitation wavelength, as is typical for Rydberg Fingerprint Spectroscopy.<sup>(18)</sup> The excitation mechanism is not fully understood but it must involve multiphoton excitation and efficient coupling to a wide range of energetically accessible states. The SAMOs will be preferentially ionized on the timescale of the laser excitation (8), for reasons discussed above, and since their potential energy surface will be similar to that of the cation, the ionization transition is expected to conserve vibrational energy thus leading to a peak in the spectrum corresponding to the electronic binding energy of the SAMO. If sufficient energy has been absorbed by the valence electrons, the molecule may thermally ionize instead of undergoing direct photoionization, leading to the thermal background that is observed in the spectra (SI), before the electronic excitation has time to couple significantly to vibrational degrees of freedom.<sup>(14)</sup>

Representative examples of the photoelectron spectra are shown in Fig. 2. The full set of spectra, prior to subtraction of the thermal background are provided in Figure S1. The peaks were identified as arising from SAMOs in an earlier publication by comparing theoretical binding energies and photoelectron angular distributions with experimental photoelectron spectra.<sup>(6)</sup> The peaks appear at identical electron binding energies (upper x-axes) for all investigated laser wavelengths. The prominent peak with a binding energy of ca. 1.9 eV corresponds to the first s-SAMO band, the next peak corresponds to the first p-SAMO band (binding energy ca. 1.5 eV) and the following peak to a combination of the first d-SAMO band and second s-SAMO band that cannot be clearly distinguished in these angle-integrated spectra (binding energies of ca. 1 eV and 0.9 eV, respectively).<sup>(6)</sup>

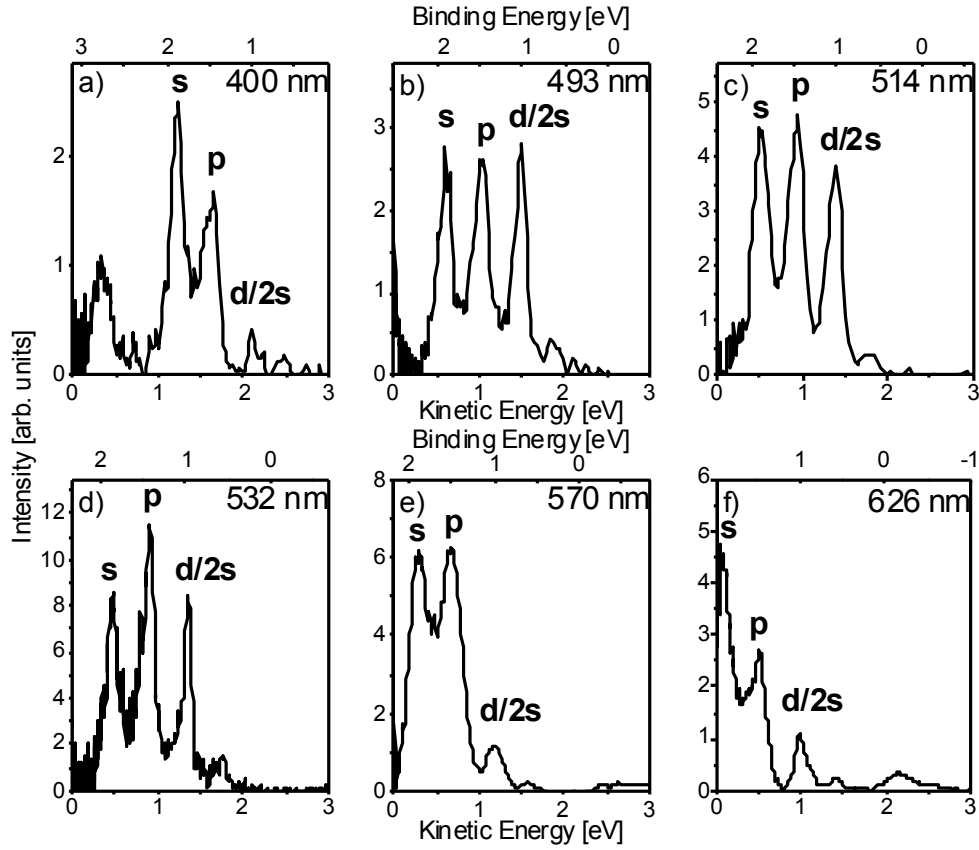


Fig. 2. One-colour fs photoelectron spectra of  $C_{60}$  at selected wavelengths after thermal electron background subtraction. The spectra are plotted in terms of both electron kinetic energy (lower axis) and electron binding energy (upper axis). The binding energy is defined as the difference between the photon energy and the photoelectron kinetic energy. Peaks corresponding to ionization from the s, p and d/2s SAMOs are marked.

In Fig. 3, the calculated photoionization widths of the lowest SAMO states are plotted as a function of photoelectron kinetic energy. The photoionization width (rate) decreases strongly as the photoelectron kinetic energy increases up to a photoelectron kinetic energy of 2eV, in

contrast to the calculations for the non-SAMO states (8) (not shown) that show an increasing photoionization width (starting from a much lower value), in agreement with identified trends found in absolute photoionization cross-section measurements for different molecular systems.(19-22) The ionization widths (rates) are predicted to be similar for the SAMO and non-SAMO states for photoelectron energies beyond 2.5 eV, converging to a value of  $\leq 0.01$  eV.(8) However, this corresponds to a photoionization lifetime that is greater than 300 fs, significantly longer than the laser pulse duration, and one would not expect to see clear peak structure in the spectra, in agreement with the experimental results in Fig. 2 and S1.

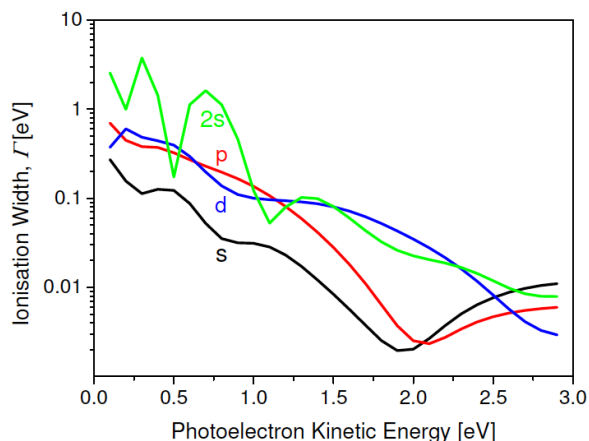


Fig. 3. Calculated photoionization widths as a function of photoelectron kinetic energy for the lowest-lying SAMO states (black = s, red = p, blue = d, green = 2s) using TD-DFT. For more details of the theoretical methods see Ref 8.

We are unable to determine absolute photoionization cross sections in the experiment. However, the ratio of the SAMO intensities can be used to compare with the corresponding ratios of the calculated photoionization widths for each value of the photon energy. Note that the photoelectron kinetic energies are different for ionization from the different SAMO states in each experiment (carried out with a fixed photon energy).

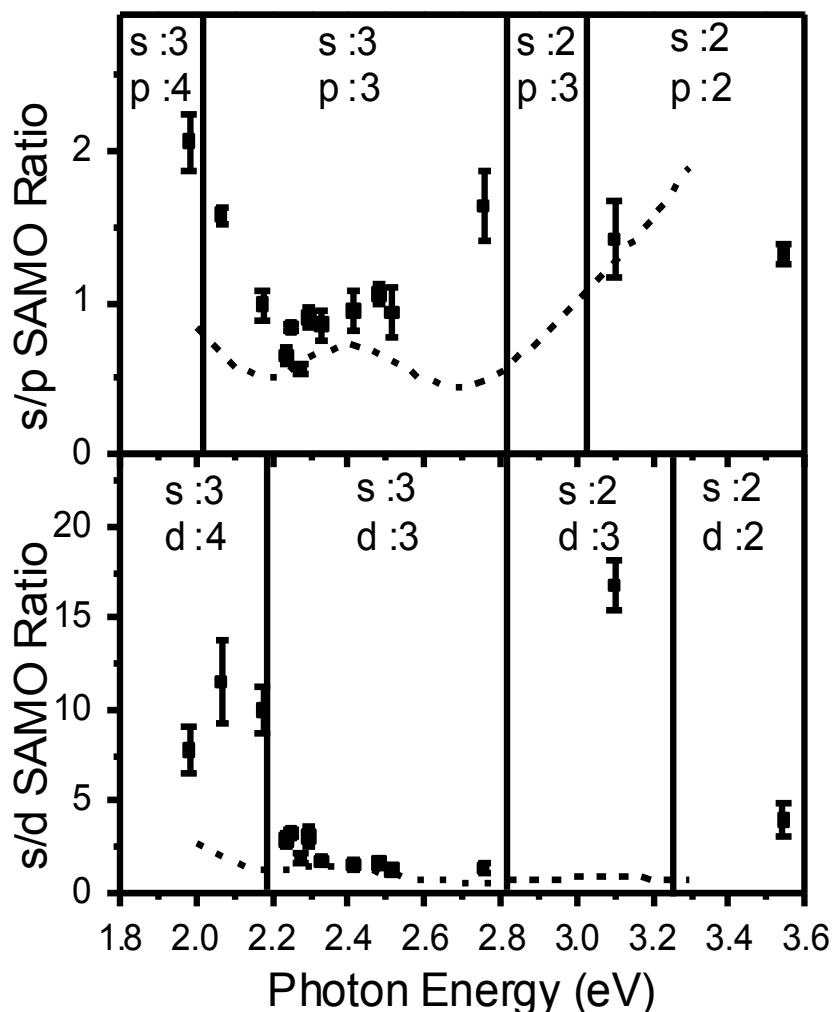


Fig. 4. Comparison of relative experimental SAMO peak intensities (squares) and the theoretical photoionization width ratios of SAMO states plotted as a function of laser photon energy. Upper panel: ratio of the s and p peak intensities; Lower panel: ratio of the s and d peak intensities. Theoretical values shown by dashed lines (ratio of average values calculated for each band).<sup>8</sup> The numbers at the top of the plots indicate the number of photons needed to access the s and the p or d SAMO states, respectively (not taking into consideration the substantial amount of vibrational energy that is present in the hot fullerenes from the oven).

Fig.4 shows the results of this comparison of the measured ratios with the predicted ratios of the s to p and s to d SAMO intensities, computed as the ratio of the ionization widths of the SAMO states.(8) There is a clear correlation between the predicted trend and the experimentally measured results within the regions where the excited states can be accessed by the *same number of photons*. Outwith these regions, the s-band can be accessed by one less photon than the higher states. In this case the s-band intensity would be expected to be significantly higher than the higher-lying states and the measured ratios are correspondingly higher. This subtlety is not predicted by the calculations since they do not include the population mechanism but simply assume that all states are populated with the same probability. The results are quite remarkable in that they are implying that this assumption (at least for the SAMO population) does hold as long as the photon order needed to energetically access the states is the same. What is apparent is that these calculations are, with surprisingly good accuracy, able to predict the photoionization probability in addition to the photoelectron angular distribution as a function of kinetic energy as shown earlier.(8)

The experimental ratios for the d and 2s SAMO peaks do not agree so well with the calculations (Fig. S8). These states have similar binding energies and thus would be accessed by the same number of photons throughout the range investigated. Here, the experimentally determined d-peak intensity is considerably larger than the 2s whereas the calculations predict very similar intensities for these two peaks. It should also be noted however that the d and 2s peaks are very difficult to distinguish in the experimental spectra and also that the calculations indicate strong oscillations in the 2s photoionization width (Fig. 3). The assignment of the 2s peak is based on the determined angular distribution.(6)

## Conclusion

The fs photoelectron spectra of  $C_{60}$  have been reported for different laser wavelengths. The experimentally determined intensity ratios of the s, p and d SAMO features in the spectra can be reproduced by taking the ratios of the photoionization widths, predicted using TD-DFT. The success of this theory at predicting the ionization properties of a system that is as large and complex as a fullerene is remarkable and provides confidence in the predictive potential of quantum chemistry techniques for probing the electronic dynamics of complex molecular systems.

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## Supporting Information Available:

Additional content providing all photoelectron spectra used for the analysis prior to subtraction of the thermal background contribution, test of relative SAMO photoionization peak intensities as a function of various experimental parameters (laser pulse duration, oven temperature, laser pulse intensity) and the comparison of the experimental peak intensity and theoretical photoionization width ratios for the d and 2s SAMOs.

This material is available free of charge via the Internet <http://pubs.acs.org>.

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## TOC Graphic

